Feb. 13, 1945. N. K. CHANEY 2,369,281

PRODUCTION OF VALUABLE HYDROCARBONS

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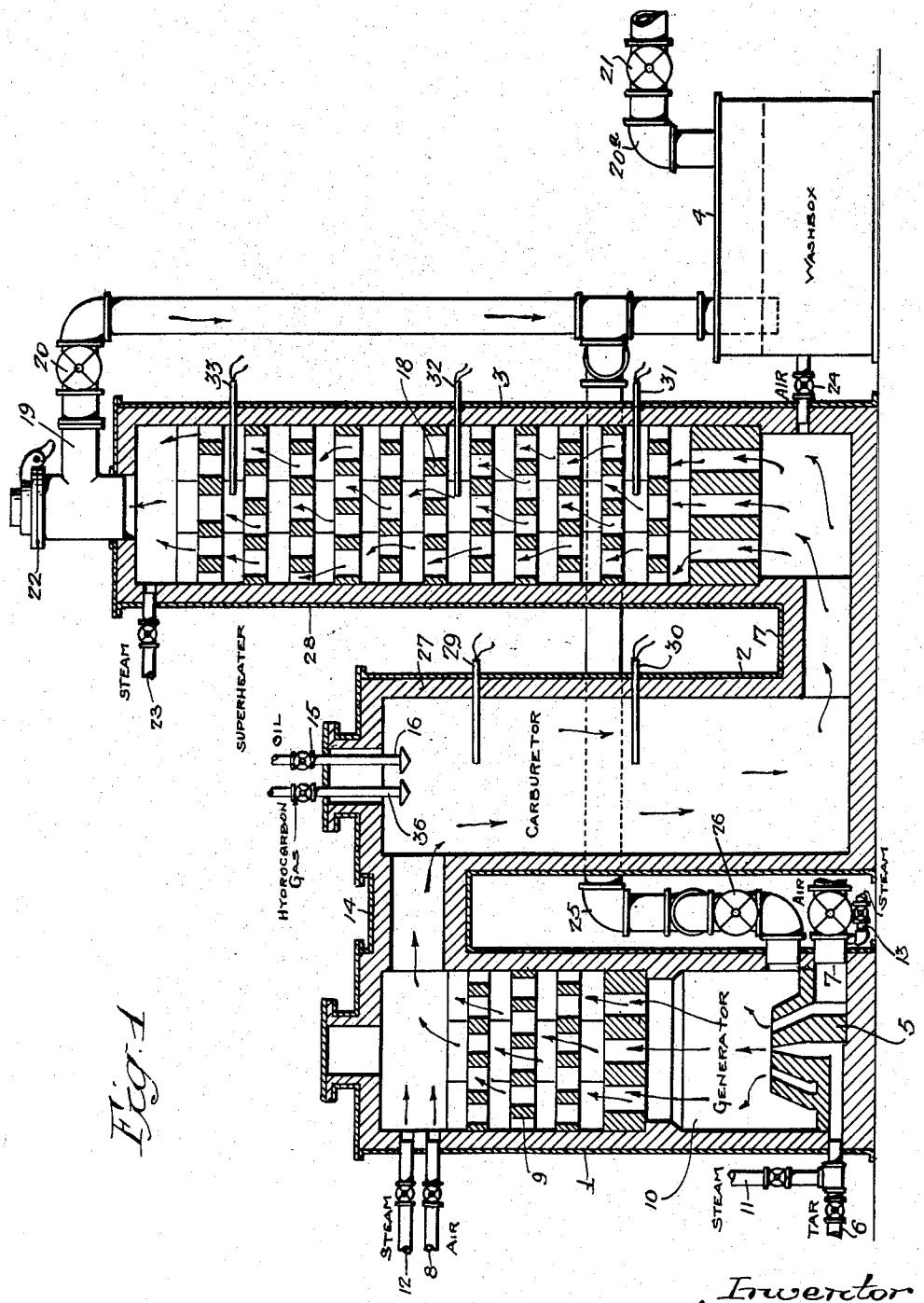


Fig. 1

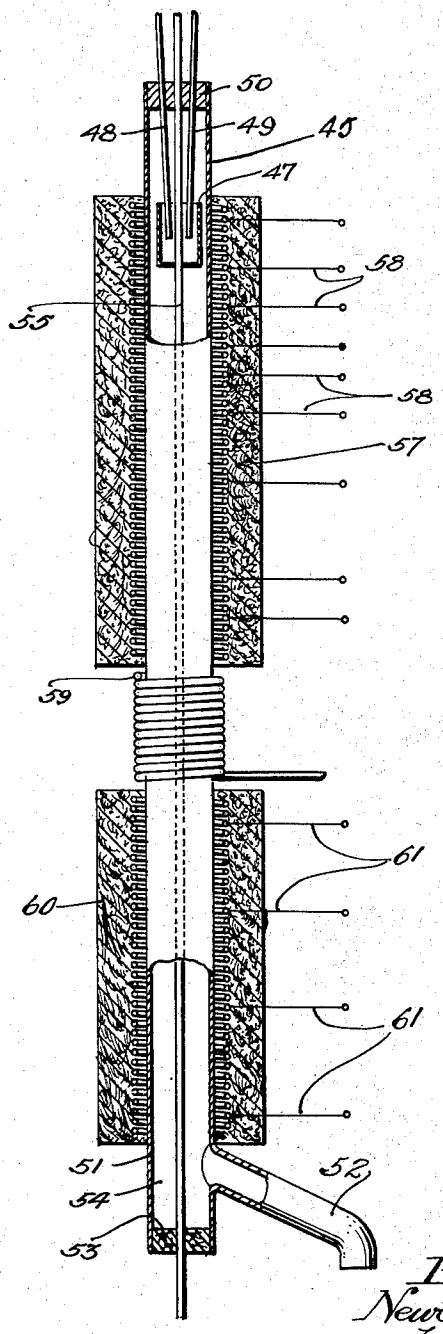
Inventor
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Fig. 2.



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2,369,281

PRODUCTION OF VALUABLE HYDROCARBONS

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Application December 28, 1940, Serial No. 372,042

12 Claims. (Cl. 260—680)

This invention pertains generally to the production of valuable hydrocarbons from petroleum oil by pyrolysis.

The invention involves the production of non-aromatic resin-forming hydrocarbons such as isobutylene; the dienes, butadiene, cyclopentadiene, dicyclopentadiene, isoprene and piperylene; non-alkylated aromatic hydrocarbons such as benzene, naphthalene and anthracene, alkylated aromatic hydrocarbons such as toluene and xylene, alkenated aromatic hydrocarbons such as styrene, methyl styrene and indene, as well as other aromatic hydrocarbons boiling above 200° C. at atmospheric pressure and comprising dead oil and heavy tars.

Normally in the manufacture of oil gas, petroleum oil is pyrolytically decomposed at high temperatures and frequently under conditions of reduced partial pressures resulting from the presence of large volumes of other gases such as steam or water gas, the latter being a mixture of carbon monoxide and hydrogen. The products range all the way from hydrogen and normally gaseous hydrocarbons which are condensible with difficulty to materials of extremely low vapor pressure, such as the less volatile constituents of tar, for example, pitch. A considerable quantity of carbon may also be produced.

These prior art processes are conducted with either of two purposes in mind, namely, (1) the production of large volumes of combustible gas to be distributed as city gas, or (2) the production of motor fuel.

In both instances, the desideratum is to conduct the decomposition of the petroleum oil so as to avoid the production of large quantities of resin-forming hydrocarbons.

In the case of combustible gas for distribution, the presence of relatively large quantities of resin-forming hydrocarbons is highly undesirable since these hydrocarbons have a propensity to form resins throughout the gas distribution system and are responsible for the stoppage of gas appliance valve orifices, causing the extinction of burners such as pilot burners and the malfunctioning of automatic appliances.

Likewise in the case of motor fuels, the presence of resin-forming hydrocarbons is highly undesirable because of their interference with the proper operation of internal combustion engines.

This invention as distinguished from the processes of the prior art is directed to the production of a relatively larger total quantity of the resin-forming hydrocarbons, particularly non-aromatic resin-forming hydrocarbons such as the dienes.

In my copending application Serial Number 220,649, filed July 22, 1938 which has matured into Patent 2,226,531, dated December 31, 1940, I have described and claimed a cyclic process for making combustible gas which as practiced in a gas-making set includes in the cycle internally preheating said gas-making set and a gas-making run involving the vapor phase cracking of petroleum oil in which the yield of valuable hydrocarbons, including alkylated and alkenated aromatic hydrocarbons is increased by introducing benzene into said gas-making set in addition to said petroleum oil during the vapor phase cracking of said petroleum oil.

Other materials and particularly alkylated benzenes may be introduced along with the benzene in the above process.

This application is a continuation-in-part of my above mentioned copending application and is more particularly addressed to the introduction of hydrocarbons of 2 and 3 carbon atoms and particularly unsaturated hydrocarbons into the gas-making set in addition to said petroleum oil during the vapor phase cracking of said petroleum oil.

In carrying out the invention, the petroleum oil is pyrolytically decomposed in vapor phase in the presence of one or more of the above substances and preferably in the presence of a substantial quantity of diluent gas which is preferably readily condensible such as steam and which is preferably present in sufficient quantity to materially reduce the partial pressures of the hydrocarbon vapors present. Preferably, the diluent is supplied in a volume equivalent to at least one part of steam to three parts of petroleum oil by weight. In any event the volume of diluent before condensation to volume of final gas remaining after condensation down to approximately atmospheric temperature should be at least 30%. A part or all of the diluent may comprise methane and/or other residual gas constituents for the most part of less than 4 carbon atoms.

While water gas may be employed as a diluent it is preferred not to use water gas in large quantities for this purpose. Thus, I prefer to restrict the presence of any blue water gas to below 30 cubic feet per gallon of oil pyrolyzed and more preferably to below 20 cubic feet per gallon of oil pyrolyzed, said cubic feet being taken as if measured at a pressure of 760 mm. and a temperature of 60° F.

Generally speaking, the preferred operating conditions are of a cyclic character such as is characterized by the conventional cyclic gas-making processes, although other types of operations including continuous operation are within the broad concept of the invention.

Also the process is preferably conducted with total pressures at atmospheric or near atmospheric pressure.

Broadly speaking, the process is conducted at average temperatures between 1150° F. and 1800° F. and preferably between 1400° F. and 1650° F.

For convenience the invention will be further illustrated in connection with the drawings which form a part of this specification and in which:

Figure 1 shows an elevation partly in section, diagrammatically illustrating a cyclic gas-making apparatus; and

Figure 2 shows an elevation partly in section, diagrammatically illustrating a continuous gas-making apparatus.

Referring to Figure 1—this figure illustrates diagrammatically apparatus in which the invention may be performed and comprises a cyclic gas-making set which may be conventional, or otherwise.

1 indicates a generator, 2 is a carburetter, 3 is a superheater, and 4 is a wash box. The generator 1 is provided with a burner generally indicated at 5 with means for supplying fluid fuel such as tar, generally indicated at 6, and with means for supplying air for combustion of the fuel generally indicated at 7. The generator may be provided with secondary air supply means as at 8. 9 indicates checkerbrick arranged above the combustion space 10. 11, 12, and 13 are steam supply pipes.

The generator 1 is connected at its upper portion to the upper portion of the carburetter 2 by connection 14. The carburetter is illustrated as devoid of checkerbrick and is provided with oil supply means 15 provided with a nozzle 16 capable of finely atomizing the oil.

The carburetter 2 is connected at its base with the base of the superheater 3 by connection 17.

The superheater 3 is shown provided with the checker brick indicated conventionally at 18. Offtake 19 provided with valve 20 leads from the top of the superheater to the wash box 4, from whence connection 20a provided with valve 21 leads to condensate recovery equipment and a gas relief holder (not shown).

The superheater is further provided with a stack valve 22 and may be provided with a steam supply means such as steam pipe 23. Air supply means such as 24 may be provided for admitting tertiary air to the superheater.

The generator 1 may be provided with the gas offtake 25 provided with valve 26 and leading from the lower portion of the generator 1 to the wash box 4.

The carburetter may be provided with checkerbrick as well as the superheater.

Other fluid fuel than tar may be employed for heating the generator 1, such for instance, as oil or gas. Further, the generator may be provided with a grate and solid fuel burned thereon for heating instead of fluid fuel, if desired.

Thermocouples such as the shielded thermocouples 29, 30, 31, 32 and 33 may be provided at spaced intervals through the vaporizing and cracking chambers, their connections leading to temperature recorders (not shown).

An illustrative cycle of operation of the apparatus of Figure 1 will be given.

In operation of the apparatus of Figure 1, fluid fuel such as tar, oil or gas is admitted to the generator burner 5 and burned in the generator, with air supplied through pipe 7. Secondary air may be supplied through air supply pipe 8. The burning products pass from the generator to the carburetter 2 by way of connection 14 and thence through the carburetter to the superheater by way of connection 17. Tertiary air may be supplied through air supply means 24, if desired. The combustion products pass through the superheater and through the stack valve 22 to atmosphere or to a waste heat boiler (not shown). During this operation, the stack valve 22 is open and valves 20 and 26 are closed.

This operation, termed the blow, heats and stores heat in the checkerbrick and lining of the generator, the lining of the carburetter and the checkerbrick and lining of the superheater.

The tar may then be shut off and a short air purge made by air admitted through air supply means 7, followed by a short steam purge with steam supplied to the base of the generator as at 13. The purged products pass out of the set through the stack valve 22.

After the set is purged, and with the stack valve 22 closed, valve 26 closed, and valves 20 and 21 open, petroleum oil is admitted to the carburetter top and finely atomized by the nozzle 16. Simultaneously, C_2 hydrocarbon material and/or C_3 hydrocarbon material is admitted to the carburetter through the nozzle 36. At the same time, steam is admitted to the generator through the steam supply in the generator base, heated in passage through the generator checkerbrick and passed into the carburetter top by way of connection 14. A portion or all of the steam may be admitted through the steam supply means 12 at the generator top above the checkerbrick instead of through 13 at the bottom and/or the temperature of the steam may be controlled by proportioning the quantities admitted to the two portions of the generator, or otherwise.

The oil is vaporized in the carburetter in the presence of the hydrocarbon additive and the superheated steam from the generator, the quantity of steam being sufficient to materially reduce the partial pressures of the hydrocarbon vapors.

The vaporized oil and hydrocarbon additive and the steam pass down through the carburetter and into the superheater through connection 17. Some pyrolysis and synthesis may take place in the carburetter.

From the base of the superheater the vaporized oil, hydrocarbon additive, steam, partially cracked vapors and partially synthesized vapors pass upward through the superheater checkerbrick in which the desired pyrolysis and synthesis are completed.

The reaction products and steam pass through connection 19, the wash box 4, and connection 20a to a relief holder (not shown) and through condensing or other apparatus (not shown) for the removal of the desired products from the gas.

After this operation, termed the run, the oil and hydrocarbon additive admission may be discontinued and the reaction products purged from the set by steam admitted to the generator, the reaction products being purged into the relief holder through the wash box.

The cycle may then be repeated. The above cycle is merely illustrative, and it may be very greatly modified. For instance, a backrun with steam, or steam and oil, or steam and oil and hydrocarbon additive may be made during the cycle,

with steam, or steam and oil, or steam and oil and hydrocarbon additive supplied through supply means 23, or otherwise. In such case, the stack valve 22 is closed, valve 20 is closed and valve 26 open. The steam, or steam and oil vapors, or steam and oil and hydrocarbon additive vapors and reaction products pass reversely through the superheater, carburetter and generator and through connection 25 to the wash box and to the relief holder (not shown).

The fluid fuel burner as a means of providing heat during the blow is preferred, but recourse might be made to the use of a solid fuel bed as in the conventional water gas generator, with the difference that it is preferred not to pass any large quantity of water gas through the carburetter and superheater during the oil cracking period. Other means for superheating steam for the process might be then employed, or saturated steam employed. The use of superheated steam, however, is preferred as it reduces the heating load on the carburetter.

During the blow, the operation is conducted to obtain the desired distribution of heat throughout the carburetter and superheater.

The following table will illustrate a typical swing in temperature at various points in a given set during a typical blow. The temperatures were determined by the standard shielded type of thermocouple.

Table 1

Point in set	Temperature °F. start of blow	Temperature °F. end of blow
Carburetter top	1,400	1,730
Carburetter middle	1,423	1,657
Superheater base	1,425	1,575
Superheater middle	1,498	1,532
Superheater top	1,500	1,510
Avg. set temperature	1,525	

The temperature gradient throughout the set will vary with operating conditions and the nature and size of the set and the set lining and checkerbrick or other heat storage material.

The temperature gradient naturally set up by the blow may be modified prior to the run by the injection of steam of other fluids to the top of the carburetter and/or the base and/or top of the superheater and/or to the generator, and/or otherwise. It may be employed to remove peak temperatures as described and claimed in copending application Serial Number 191,441, filed February 19, 1938, by Edwin L. Hall.

The point or points of introduction of the oil or hydrocarbon additive may vary in the same or different gas making equipment, from those chosen for illustration.

The oil whether coming into contact with refractory surfaces in significant quantity or not is subjected to the temperatures of the carburetter and superheater and is decomposed in the presence of the hydrocarbon additive, and steam.

The temperatures given above are illustrative in character.

The above is a description of a conventional cycle chosen for illustration except that hydrocarbon additive is introduced into the oil pyrolyzing environment. Any other appropriate cycle might be substituted.

After passing through the offtake 19 the gas is passed through a relief holder and then through water cooled condensers or vice versa to the purifiers for the removal of hydrogen sulfide and may then be further treated for the removal of lower boiling hydrocarbons therefrom.

The wash box 4 in which the gas comes into contact with water and the water cooled condensers cool the gas down to an appropriate or desired temperature which is usually atmospheric or somewhat above. As a result the tar separates as condensate from the gas. This tar may be considered roughly as being composed of three portions, namely, light oil which may be considered as that portion boiling up to say approximately 200° C., dead oil which may be considered as that portion boiling between say approximately 200° C. and 350° C. or higher, and residual tar.

The light oil fraction contains substantially all of the indene, dicyclopentadiene, methyl styrene, the larger part of the styrene, xylene and toluene, a large part of the benzene and other miscellaneous hydrocarbons such as "benzol forerunnings." The individual hydrocarbons may be recovered from light oil by any suitable means, for example, fractional distillation.

Usual gas practice does not carry the condensation further.

To recover from the gas lower boiling hydrocarbons such as the rest of the styrene, xylene, toluene and benzene, cyclopentadiene, piperylene, isoprene, butadiene and butylenes, special measures are employed to effect condensation of which refrigeration, compression, absorption and adsorption or any combination thereof are examples.

The individual hydrocarbons may be separated from the condensate by various means which frequently involve fractional distillation.

Examples of hydrocarbons of 2 and 3 carbon atoms which may be introduced into the oil pyrolyzing environment are ethylene, ethane, propylene, and propane, or combinations of these materials with or without other gaseous substances such as methane and hydrogen normally occurring in residual gas as well as small quantities of C_4 hydrocarbons and higher.

The term "residual gas" as herein employed is to be construed as that portion of the gas from which substantially all of the hydrocarbons of five and six carbon atoms have been removed and from which preferably at least the larger part of the butadiene has been removed. As an example, a sample of residual gas suitable for employment in this process showed upon analysis C_2H_4—22.3%; C_2H_6—3.8%; C_3H_6—5.8%; C_3H_8—0.4%; C_4 and higher—1.6%; CH_4—31.5%; H_2—23.4%; CO—2.0%; CO_2—3.4%; O_2—0.6%; and N_2—5.2%.

"Ethylene" when used in the form of residual gas is preferably present in a concentration of at least 15% by volume. Propylene under like circumstances is preferably present in a concentration of at least 2% by volume.

All or any part of the C_2 and C_3 hydrocarbons produced in the cracking operation such as the overall residual gas or ethylene and/or propylene fractions thereof may be separated from the products of pyrolysis and recycled through the pyrolyzing apparatus together with the petroleum oil.

The recycled hydrocarbon additive or hydrocarbon additive otherwise obtained, if desired, may be mixed such as under pressure with the petroleum oil prior to admission to the pyrolyzing apparatus as through supply means 15 of Figure 1. However, as temperatures in the cracking apparatus, such for instance, as in the car-

buretter and superheater above described may be considerably varied with variations in the cycle and method of operation, it may not be desirable to introduce the additive at the point of admission of petroleum oil, as the zone of maximum free radical production will necessarily vary with the variation in temperature distribution.

The oil gas apparatus and cycle earlier described were given merely for convenience in illustrating the apparatus and process adapted for use with my invention and are subject to very wide modifications.

Referring now to Figure 2 wherein cracking apparatus of the continuous or continual type is illustrated on a laboratory scale, 45 comprises a reaction tube which may be any suitable material such as quartz, or any of the materials employed in continuous or continual cracking operations.

Tube 45 at its inlet end is shown provided with a baffle 47 in the form of a cup into which project hydrocarbon feeding tube 48 and steam feeding tube 49. Feeding tubes 48 and 49 pass through and form a gas-tight fit with a closure member 50 for the inlet end of tube 45.

Tube 45 adjacent its outlet end 51 is provided with a gas delivery side arm 52 and a closure member 53, the latter being sufficiently below side arm 52 to form a well 54.

Tube 45 is also shown provided with an axially arranged tube 55 of small diameter. Tube 55, as shown, projects through closure members 50 and 53 and provides a convenient way of arranging thermocouple junctions for the measure of temperature. Tube 55 may be of any convenient material, such as quartz, or any other material suitable for continuous or continual cracking purposes.

Tube 45 may be of any convenient length which is usually correlated with the provisions for feeding steam and additive and for feeding and vaporizing oil in order to make it possible to obtain times of contact within a desired range.

For temperature control purposes, tube 45 is shown surrounded with a heating member 57 in the form of a resistance winding which may be provided with several taps, as illustrated at 58; a cooling coil 59 of tubular construction for the flow of cooling fluid; and another resistance winding 60 provided with suitable taps, illustrated at 61.

It will be seen that the provision of a cooling coil 59 between resistance windings 57 and 60, and the provision of taps 58 and 61 on windings 57 and 60 respectively, make it possible to closely control temperature conditions within tube 45 as well as to vary such conditions along tube 45, if and as desired.

Assuming that heaters 57 and 60 and cooler 59, if necessary, are operating to establish desired temperature conditions within tube 45, the operation of the apparatus shown in Figure 2 is as follows:

Oil is fed through tube 48 and steam and gaseous hydrocarbon additive are fed through tube 49. These materials strike baffle 47 thus becoming mixed. The resulting reduction in partial pressures of hydrocarbon vapors and the surrounding temperatures are ordinarily sufficient to vaporize all of the hydrocarbons present.

The vaporized hydrocarbons in passing through tube 45 in the presence of steam or other diluent are pyrolyzed and synthesized in a manner similar to that already described in connection with Figure 1.

Because of the temperatures involved substantially all of the materials except some free carbon remain in the vapor phase and pass off through delivery arm 52 with the gas. The tar and lower boiling condensates may be separated from the gas in any desired manner, for example, as already described in connection with Figure 1.

The following table will illustrate typical temperatures at various points in tube 45 during the practice of my invention. The temperatures at the various points were determined by inserting thermocouples in tube 55.

Table 2

Point in tube	Average temperature, °F.
Entrance to tube	600–900.
Above cooling coil 59 (main pyrolyzing zone).	1,150–1,800. Preferably 1,400–1,650.
In cooling coil 59	Below 1,100.
Below cooling coil 59	Below 800.

It may be desirable to have the section of the tube below cooling coil 59 relatively short or to operate it at a temperature above 1150° F. to obtain extended times of contact, in which case cooling coil 59 would usually be inoperative.

Thus as particularly described, the portion of the tube 45 above the cooling coil 59 constitutes the chief pyrolyzing chamber, and the portion of the tube below the cooling coil 59 is maintained at a temperature sufficiently high to avoid condensation of heavy tars whether or not such temperature is sufficiently high to substantially prolong the pyrolysis.

The apparatus in Figure 2 is of course largely for illustration and may be replaced by a plant size unit or units.

If desired, tube 45 may contain refractory material of suitable size and shape, particularly if sufficient free space is afforded for the flow of vapors, such additional refractory materials providing additional contact surfaces.

Any other heating means may be added or substituted.

Small amounts of free carbon or other non-vaporizable substances tend to collect in well 54 from which they may be removed during cleaning by removal of closure member 53.

When the walls of tube 45 become coated with a layer of carbon sufficiently thick to interfere with proper heat exchange, or otherwise, it may be removed by any suitable means, such as by passing air or oxygen in through tube 48 or 49, or both, the products of combustion being removed through side arm 52.

As an example of increased yields of valuable hydrocarbons in the laboratory apparatus of Figure 2, the following may be given.

A crude oil and approximately 38% by weight of residual gas substantially free from hydrocarbons of more than two carbon atoms were pyrolyzed in the presence of each other under closely similar conditions of temperature and time of contact as a control employing 100% of the same crude oil, in a quartz tube known commercially as "Vitrosil."

The inside diameter of the tube 45 was 1⅛" and the length 34.4 inches. The outside diameter of tube 55 was 11 mm.

In each case steam was admitted with the materior pyrolyzed and synthesized. The table below shows the increased yields of certain valuable hydrocarbons especially benzene.

Table 3

	With residual gas	Without residual gas
Pounds of oil to pounds of steam	1.97 to 1	1.21 to 1
Avg. temperature above baffle 47....°F.	528	835
Time of contact above baffle 47..seconds..	.290	.289
Avg. temperature between baffle 47 and cooling coil 59....°F.	1,540	1,512
Time of contact between baffle 47 and cooling coil 59....seconds..	.932	.697
Avg. temperature of cooling coil section....°F.	1,040	1,093
Time of contact in cooling coil section seconds..	.188	.322
Avg. temperature below cooling coil..°F..	751	756
Time of contact below cooling coil..seconds..	1.396	1.129
Benzene #/gal. oil pyrolyzed	.735	.569
Napthalene #/gal. oil pyrolyzed	.037	.015
Styrene #/gal. oil pyrolyzed	.083	.078
Residual gas (gross) #/gal. oil pyrolyzed	5.622	3.198

As an example of increased yields of valuable hydrocarbons in the same apparatus employing as additive residual gas not stripped of C_3 hydrocarbons but substantially free from hydrocarbons of four carbon atoms, the following may be given.

A crude oil and 42% of its weight of said residual gas were pyrolyzed in the presence of each other under closely similar conditions of temperature and time of contact as the control of Table 3.

In each case steam was admitted with the material pyrolyzed. The table below shows the increased yields of certain valuable hydrocarbons, especially butadiene and benzene.

Table 4

	With residual gas	Without residual gas
Pounds of oil to pounds of steam	1.7 to 1	1.2 to 1
Avg. temperature above baffle 47....°F.	670	835
Time of contact above baffle 47..seconds..	.270	.289
Avg. temperature between baffle 47 and cooling coil 59....°F.	1,509	1,512
Time of contact between baffle 47 and cooling coil 59....seconds..	.987	.697
Avg. temperature cooling coil section..°F.	991	1,093
Time of contact cooling coil section seconds..	.310	.322
Avg. temperature below cooling coil...°F.	749	756
Time of contact below cooling coil seconds..	1.360	1.129
Benzene #/gal. oil pyrolyzed	.677	.569
Toluene #/gal. oil pyrolyzed	.318	.289
Naphthalene #/gal. oil pyrolyzed	.021	.015
Butadiene #/gal. oil pyrolyzed	.227	.134
Isoprene and piperylene #/gal. oil pyrolyzed	.067	.051
Residual gas #/gal. oil pyrolyzed (gross)	6.218	3.198

As another example a mixture of the crude oil of Table 4 and 8.3% of its weight of ethylene (alone) were pyrolyzed together under similar conditions of temperature and time of contact as a control employed said crude oil alone. The following table shows the results.

Table 5

	With Ethylene	Without Ethylene
Pounds of oil to pounds of steam	1.10 to 1	1.09 to 1
Avg. temperature above baffle 47....°F.	826	616
Time of contact above baffle 47..seconds..	.291	.249
Avg. temperature between baffle 47 and cooling coil 59....°F.	1,647	1,539
Time of contact between baffle 47 and cooling coil 59....seconds..	.737	.859
Avg. temperature cooling coil section..°F.	1,128	1,044
Time of contact cooling coil section seconds..	.233	.262
Avg. temperature below cooling coil...°F.	751	749
Time of contact below cooling coil seconds..	1.118	1.197
Benzene #/gal. oil pyrolyzed	1.057	.648
Toluene #/gal. oil pyrolyzed	.237	.189
Naphthalene #/gal. oil pyrolyzed	.106	.074
Styrene #/gal. oil pyrolyzed	.08	.075
Methyl styrene #/gal. oil pyrolyzed	.076	.042
Residual gas #/gal. oil pyrolyzed (gross)	3.783	3.192

As an example of the use of propylene alone as additive with apparatus of the character shown in Figure 2, the following may be given.

The crude oil of Table 5 and 11.4% of its weight of propylene (alone) were pyrolyzed together under similar conditions of temperature and time of contact as the control of Table 5. The results are given in the following table.

Table 6

	With propylene	Without propylene
Pounds of oil to pounds of steam	1.07 to 1	1.09 to 1
Avg. temperature above baffle 47....°F.	746	616
Time of contact above baffle 47..seconds..	.325	.249
Avg. temperature between baffle 47 and cooling coil 59....°F.	1,545	1,539
Time of contact between baffle 47 and cooling coil 59....seconds..	.772	.859
Avg. temperature cooling coil section..°F.	1,082	1,044
Time of contact cooling coil section seconds..	.251	.262
Avg. temperature below cooling coil..°F.	735	749
Time of contact below cooling coil seconds..	1.183	1.197
Benzene #/gal. oil pyrolyzed	.760	.648
Toluene #/gal. oil pyrolyzed	.214	.189
Solvent naphtha #/gal. oil pyrolyzed	.245	.178
Dead oil #/gal. oil pyrolyzed	.645	.403
Butadiene #/gal. oil pyrolyzed	.142	.100
Cyclopentadiene (and dimer) #/gal. oil pyrolyzed	.081	.047
Isoprene and piperylene #/gal. oil pyrolyzed	.097	.053
Methyl styrene #/gal. oil pyrolyzed	.060	.042
Residual gas (gross) #/gal. oil pyrolyzed	3.501	3.192

The foregoing examples clearly demonstrate the advantages of my process in the production of valuable hydrocarbons.

Various modifications thereof are possible.

It will, of course, be understood that the apparatus of Figures 1 and 2 has been particularly described for the purposes of illustration and that many forms of apparatus may be substituted therefor.

In the claims the term "petroleum oil" is intended to have the meaning commonly accepted in the art, namely crude oil and physically separated fractions thereof.

It will also be understood that changes, omissions, additions, substitutions and/or modifications may be made within the scope of the claims without departing from the spirit of the invention.

I claim:

1. In a process for making valuable unsaturated resin-forming hydrocarbon material which involves the vapor phase pyrolysis of petroleum oil, the steps of increasing the recovery of unsaturated resin-forming hydrocarbon material comprising conducting said pyrolysis of petroleum oil under pressure conditions not widely departing from atmospheric pressure and in the presence of added normally gaseous hydrocarbon material selected from the group consisting of (1) an ethylene fraction of the normally gaseous products of petroleum oil pyrolysis and (2) a propylene fraction of the normally gaseous products of petroleum oil pyrolysis, and separating said unsaturated resin-forming hydrocarbon material from the products of said vapor phase pyrolysis.

2. In a process for making valuable unsaturated resin-forming hydrocarbon material which involves the vapor phase pyrolysis of petroleum oil, the steps of increasing the recovery of unsaturated resin-forming hydrocarbon material comprising conducting said pyrolysis of petroleum oil in the presence of added normally gaseous hydrocarbon material selected from the group

consisting of (1) an ethylene fraction of the normally gaseous products of petroleum oil pyrolysis and (2) a propylene fraction of the normally gaseous products of petroleum oil pyrolysis, and separating said unsaturated resin-forming hydrocarbon material from the products of said vapor phase pyrolysis.

3. In a process for making valuable unsaturated resin-forming hydrocarbon material including unsaturated resin-forming aromatic hydrocarbon material which involves the vapor phase pyrolysis of petroleum oil, the steps of increasing the recovery of said unsaturated resin-forming aromatic hydrocarbon material comprising conducting said pyrolysis of petroleum oil in the presence of an added quantity of an ethylene fraction separated from the normally gaseous products of petroleum oil pyrolysis.

4. In a process for making valuable unsaturated resin-forming hydrocarbon material including conjugated diolefine material which involves the vapor phase pyrolysis of petroleum oil, the steps of increasing the recovery of said conjugated diolefine material comprising conducting said pyrolysis of petroleum oil in the presence of an added quantity of a propylene fraction separated from the normally gaseous products of petroleum oil pyrolysis remaining after removal of butadiene, and separating conjugated diolefine material from the products of said vapor phase pyrolysis.

5. In a cyclic process for the production of valuable resin-forming unsaturated hydrocarbon material including resin-forming unsaturated aromatic hydrocarbon material involving the storing of heat in heat storage material by the combustion of heating gases during a heating portion of the cycle and the employment during a petroleum oil pyrolyzing portion of the cycle of said stored heat for the vapor phase pyrolysis of petroleum oil, the steps of favoring an increased recovery of said resin-forming unsaturated aromatic hydrocarbon material which comprise conducting said vapor phase pyrolysis by said stored heat under temperature conditions between 1150° F. and 1800° F. in the presence of an added quantity of an ethylene fraction separated from the normally gaseous products of petroleum oil pyrolysis, and separating resin-forming unsaturated aromatic hydrocarbon material from the products of said vapor phase pyrolysis.

6. In a cyclic process for the production of valuable resin-forming unsaturated hydrocarbon material including conjugated diolefine material involving the storing of heat in heat storage material by the combustion of heating gases during a heating portion of the cycle and the utilization during a petroleum oil pyrolyzing portion of the cycle of said stored heat for the vapor phase pyrolysis of petroleum oil, the steps of favoring an increased recovery of said conjugated diolefine material which comprise conducting said vapor phase pyrolysis by said stored heat in the presence of an added quantity of a propylene fraction separated from the normally gaseous products of petroleum oil pyrolysis remaining after removal of butadiene, and separating conjugated diolefine material from the products of said vapor phase pyrolysis.

7. In a cyclic process for the manufacture of valuable resin-forming unsaturated hydrocarbon material including butadiene involving the storage of heat in heat storage material by the combustion of heating gases during a heating period of the cycle and the utilization of said stored heat during a petroleum oil pyrolyzing period of said cycle for the vapor phase pyrolysis of petroleum oil, the steps of favoring an increased recovery of butadiene which comprise conducting said vapor phase pyrolysis of petroleum oil by said stored heat under temperature conditions between 1150° F. and 1800° F. in the presence of an added quantity of a propylene fraction separated from normally gaseous products of the petroleum oil pyrolysis remaining after the removal of butadiene, and separating butadiene from the products of said vapor phase pyrolysis.

8. In a cyclic process for the production of valuable resin-forming unsaturated hydrocarbon material including conjugated diolefine material of more than three and less than six carbon atoms per molecule involving the storage of heat in heat storage material by the combustion of heating gases during a heating portion of the cycle and the utilization of the stored heat in a petroleum oil pyrolyzing portion of the cycle for the vapor phase pyrolysis of petroleum oil, the steps of favoring an increased recovery of said conjugated diolefine material which comprise conducting said vapor phase pyrolysis by said stored heat in the presence of diluent steam and of an added quantity of a propylene fraction separated from the normally gaseous products of petroleum oil pyrolysis remaining after removal of butadiene, conducting said pyrolysis under temperature conditions between 1400° F. and 1800° F., and separating said conjugated diolefine material of more than three and less than six carbon atoms per molecule from the products of said vapor phase pyrolysis.

9. In a cyclic process for the production of valuable resin-forming unsaturated hydrocarbon material including conjugated diolefine material of more than three and less than six carbon atoms per molecule involving the storage of heat in heat storage material by the combustion of heating gases during a heating portion of the cycle and the utilization of said stored heat during a petroleum oil pyrolyzing portion of the cycle for the vapor phase pyrolysis of petroleum oil, the steps of recycling into the petroleum oil pyrolyzing environment during the petroleum oil pyrolyzing portion of the cycle a propylene fraction separated from the normally gaseous products of said vapor phase pyrolysis after the removal of butadiene therefrom, conducting said vapor phase petroleum oil pyrolysis under temperature conditions between 1150° F. and 1800° F. in the presence of steam and said recycled propylene fraction, and recovering said conjugated diolefine material from the products of said vapor phase pyrolysis.

10. In a cyclic process for the production of valuable resin-forming unsaturated hydrocarbon material including conjugated diolefine material of more than three and less than six carbon atoms per molecule involving the storing of heat in heat storage material by the combustion of heating gases during a heating portion of the cycle and the utilization of the stored heat during a petroleum oil pyrolyzing portion of the cycle for the vapor phase pyrolysis of petroleum oil, the steps of favoring increased recoveries of said conjugated diolefine material which comprise conducting said vapor phase pyrolysis by said stored heat under temperature conditions between 1400° F. and 1800° F. and in the presence of a quantity of added diluent gas at least equivalent to 30% of the volume of gas resulting from said pyrolysis when said resulting gas is meas-

ured at atmospheric temperature and pressure, said added diluent gas comprising steam and added normally gaseous hydrocarbon material, separately recovering said conjugated diolefine material from the products of said vapor phase pyrolysis, separately recovering a residual gas from said products substantially free from hydrocarbons of more than four carbon atoms per molecule and relatively free from conjugated diolefine material, separating a propylene fraction from said residual gas and employing said propylene fraction as a portion of said added diluent gas in said vapor phase pyrolysis.

11. In a cyclic process for the production of valuable resin-forming unsaturated hydrocarbon material including conjugated diolefine material of more than three and less than six carbon atoms per molecule involving the storing of heat in heat storage material by the combustion of heating gases during a heating portion of the cycle and the utilization of the stored heat during a petroleum oil pyrolizing portion of the cycle for the vapor phase pyrolysis of petroleum oil, the steps of favoring increased recoveries of said conjugated diolefine material which comprise conducting said vapor phase pyrolysis by said stored heat under temperature conditions between 1400° F. and 1650° F. and in the presence of a quantity of added diluent gas at least equivalent to 30% of the volume of gas resulting from said pyrolysis when said resulting gas is measured at atmospheric temperature and pressure, said added diluent gas comprising steam and added normally gaseous hydrocarbon material, separately recovering said conjugated diolefine material from the products of said vapor phase pyrolysis, separately recovering a residual gas from said products substantially free from hydrocarbons of more than four carbon atoms per molecule and relatively free from conjugated diolefine material, separating a propylene fraction from said residual gas and employing said propylene fraction as a portion of said added diluent gas in said vapor phase pyrolysis.

12. In a cyclic process for the production of valuable resin-forming unsaturated hydrocarbon material including resin-forming unsaturated aromatic hydrocarbon material involving the storing of heat in heat storage material by the combustion of heating gases during a heating period of the cycle and the utilization of the stored heat during a petroleum oil pyrolyzing portion of the cycle for the vapor phase pyrolysis of petroleum oil, the steps comprising conducting said pyrolysis under temperature conditions between 1400° F. and 1800° F. and in the presence of an added ethylene fraction separated from the normally gaseous products of pyrolysis of petroleum oil after the separation therefrom of substantially all hydrocarbon material of more than four carbon atoms per molecule and after the removal therefrom of butadiene, and separating said unsaturated resin-forming hydrocarbon material from the products of said vapor phase pyrolysis.

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